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(54) **Direct casting method for producing low-stress glass/plastic composit s**

(57) A direct casting process for the production of a low-stress composite article e.g. a lens comprising a glass element bonded to a high-shrinkage thermosetting plastic element comprises:

– coating selected surface portions of the glass element with a thermoplastic adhesive having a heat sealing temperature above the minimum curing temperature of the thermosetting plastic;

–casting the thermosetting plastic in liquid form against the surface porti ns of the glass element which have been coated with the thermoplastic adhesive;

– curing the thermosetting plastic by heating the plastic, the glass element and the thermoplastic adhesive to a temperature below the heat sealing temperature of the thermoplastic adhesive, but above the minimum curing temperature of ths thermosetting plastic;

and

– consolidating the cured thermosetting plastic, thermoplastic adhesive and glass element into a unitary glass/plastic composite by heating them to a temperature above theheat sealing temperature of the thermoplastic adhesive.

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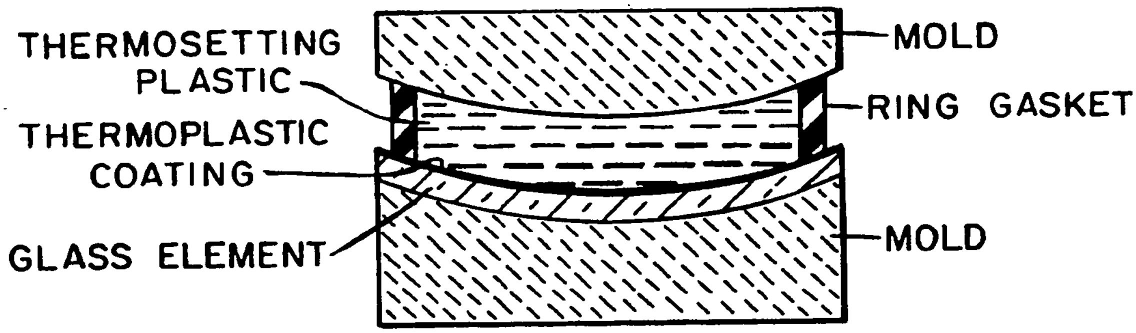

Fig. 1

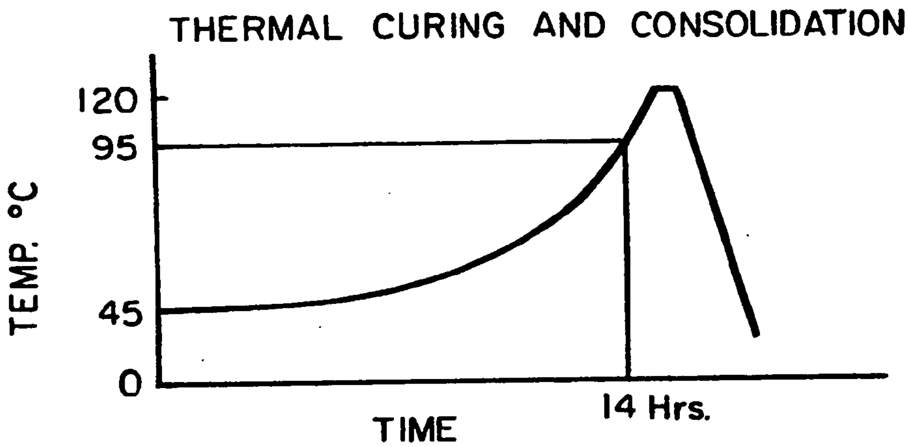

Fig. 2

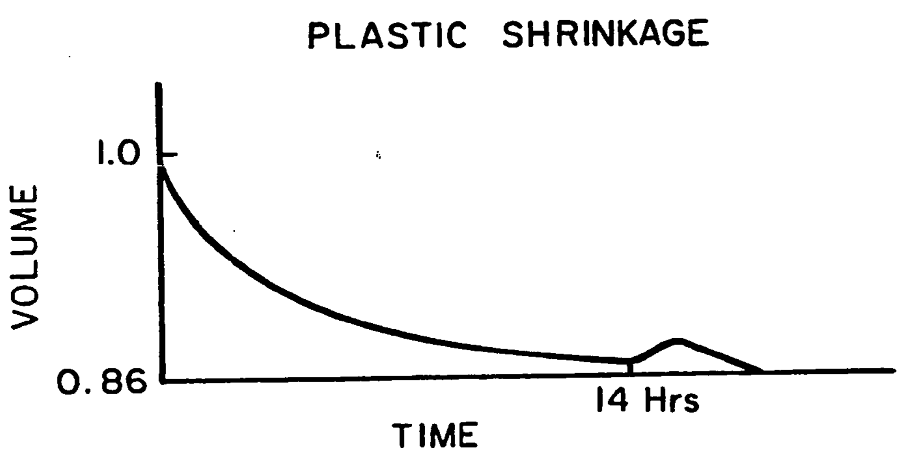

Fig. 3

SPECIFICATION

Direct casting method for producing l w-stress glass/plastic composites

This invention relates to a direct casting method for producing low-stress glass /plastic composites; more particularly, it is concerned with a process for the production of optically clear composites of laminated structure for a variety of applications.

The advantages of combining the light weight of clear plastics with the scratch resistance and chemical durability of glass having long been recognized. U.S. Patent No. 2,361,589, for example, describes durable, lightweight lenses formed by laminating thin glass sheets to the exterior of plastic lenses.

Although composite products exhibiting the desired physical properties may be produced by lamination methods, the direct moulding or casting of such composites is more efficient and thus more attractive from the commercial point of view. One procedure for adapting such direct methods to the manufacture of optical composites is described German Patent No. 1,529,861.

Among the optically clear plastics suitable for use in composites of this type are certain thermosetting plastics exhibiting high shrinkage on curing. Examples of such plastics are epoxy and allyl carbonate plastics. As suggested in U.S. Patent No. 3,382,137, curing shrinkage such as is exhibited by plastics of this type may generate very high stresses in direct cast glass/plastic composite articles.

The minimization of such stresses may be important for optical applications. For example, in the case of the plastic plastic polarizing lenses described in U.S. Patent No. 3,970,367, excess stress was found to introduce birefringence into the lenses. Careful positioning of the polarizing plastic element within the optical plastic lens body was therefore specified in order to minimize the optical affects of any residual stress.

Stress is also a problem in the case of cast glass/plastic lenses having, for example, only a front surface protected by a thin glass element. In this configuration, shrinkage of the plastic during curing may cause deformation of the lens anf cracking of the protective glass.

Some thermosetting plastics generate only moderate stress during shrinkage and then fail due to plastic cracking prior to full curing. In cast glass/plastic composites produced from these plastics, locally adhering plastic areas bounded by a network of caracks in the plastic are usually produced. Of course, such composites are useless for optical applications.

It is a principal object of the present invention to provide a direct casting method for producing composite glass/plastic articles wherein residual stresses attributable to shrinkage of the cast plastic are eliminated.

It is a further object of the present invention to provide a direct casting method which may be used for the manufacture of glass-surfaced plastic lenses exhibiting low residual stress.

In accordance with the present invention, a cast glass/plastic aritcle comprising at least one glass element indirectly bonded to a cast-in-place high-shrinkage thermosetting plastic element is provided by a method which includes a consolidation heating step subsequent to the step of curing the thermosetting plastic element of the article. A thermoplastic adhesive coating provided between the glass and plastic elements acts to control stress in the composite arising from curing shrinkage and to finally bond the glass and cured plastic elements together during consolidation. By the use of this method, glass/plastic composites comprising low curing strength plastics and/or thin glass elements surrounding or encased in plastic may be provided.

The present invention specifically comprises the initial step of coating selected portions of the glass element to be incorporated into the composite with a thermoplastic coating which may act as an adhesive. The surface portions coated are those against which the thermosetting plastic selected for the plastic element of the composite is to be cast.

Accordingly, the present invention provides a direct casting process for the production of a low-stress composite article comprising a glass element bonded to a high-shrinkage thermosetting plastic element which comprises:

- coating selected surface portions of the glass element with a thermoplastic adhesive having a heat sealing temperature above the minimum curing temperature of the thermosetting plastic;
- casting the thermosetting plastic in liquid form against the surface portions of the glass element which have been coated with the thermoplastic adhesive;
- curing the thermosetting plastic by heating the plastic, the glass element and the thermoplastic adhesive to a temperature below the heat sealing temperature of the thermoplastic adhesive, but above the minimum curing temperature of the thermosetting plastic; and
- consolidating the cured thermosetting, plastic, thermoplastic adhesive and glass element into a unitary glass/plastic composite by heating them to a temperature above the heat sealing temperature of the thermoplastic adhesive.

The present invention also relates to a composite article produced by such a process and to an optical element or system which comprises such a composite article.

It is desirable to select for the coating a thermoplastic adhesive having a heat sealing temperature above the minimum curing temperature of the thermosetting plastic which is selected. Such an adhesive remains in a relatively solid, non-reactive state during the curing of the thermosetting plastic, preventing undesirable chemical interactions and minimizing bonding and stress build-up between the plastic and the adhesive.

After selected surface portions of the glass element have been coated, the selected thermosetting plastic in liquid form is cast against the coated surface portions of the glass and the liquid plastic is then cured by heating the glass, plastic and coating to a temperature below the heat sealing tempera-

ture of the thermoplastic adhesive, but above the minimum curing temperature of the thermosetting plastic. During this step, the plastic may be held in place against the coated glass by gravity or by using for example, conventional mould elements or gaskets.

After the thermosetting plastic has been cured, the glass element, thermoplastic adhesive and cured thermosetting plastic element are further heated to a temperature above the heat sealing temperature of the thermoplastic adhesive to finally bond the cured plastic element to the adhesive-coated glass element. During this consolidation heating step, the softened thermoplastic adhesive may also release any stress generated between the glass and plastic due to curing shrinkage, thus providing an essentially stress-free glass/plastic composite article.

After consolidation has been completed, the composite article is cooled to ambient temperature. Differences in thermal expansion between the glass and plastic elements give rise to some stress in the composite as it is cooled; however, these stresses are low and thus do not ordinarily affect the physical or optical properties of the composite.

Referring to the accompanying drawings,

Figure 1 is a schematic elevational view in cross-section of one type of cast glass/plastic composite article provided in accordance with the present invention, together with mould and gasket element utilized during the casting of the article;

Figure 2 is is a graph of treating temperature versus time as a composite glass/plastic article is cycled through illustrative plastic curing and consolidation heating steps; and

Figure 3 is a graph of plastic shrinkage versus time during the plastic curing and stress-release heating steps shown in Figure 2.

The present invention is particularly useful for the production of optical elements, such as light-weight glass/plastic lenses. Although the configuration of glass elements for such lenses may vary, the elements are typically quite thin e.g. up to 0.05 cm (0.020"). They may also be spherically and/or cylindrically curved, with the degree of curvature having a direct effect upon the refracting characteristics of the lens. Nevertheless, by the proper selection of a thermoplastic coating material, the curvature characteristics of the glass element may be fully reproduced in the composite even when plastics exhibiting very high shrinkage upon curing are employed.

For applications such as lenses, it is important to use an optically clear thermoplastic adhesive to provide the thermoplastic coating on the surface of the glass element. Although the thickness of the coating is not critical, the thermoplastic must be one which may be conveniently applied in uniform thickness in order to avoid optical distortion in the product.

An example of a thermoplastic adhesive having desirable optical properties and good stress-release and heat sealing characteristics is polyvinyl butyral. Coatings of this thermoplastic may be conveniently provided on glass using plastic sheets or by coating the glass with a solution of polyinvyl butyral in a suitabl solvent by, for example, dipping, spraying, brushing or spinning. Polyvinyl butyral also has a heat sealing temperature sufficiently high to remain essentially non-adhesive at ths curing temperatures of several optical-quality, high-shrinkage thermosetting plastics. For the present purposes, the "heat sealing temperature" is that temperature at which the thermoplastic becomes soft and/or reactive enough to bond to ths thermosetting plastic.

Among the thermosetting plastics having desirable optical properties for lens applications are the allyl diglycol carbonate plastics, e.g. a plastic produced from diethylene glycol bis (allyl carbonate) resin. This resin, commercially available and commonly known as "CR-39" resin, typically exhibits a shrinkage on curing of about 14% by volume. It has a minimum curing temperature of about 70°C (f r soft cure), and is ordinarily heated to a peak curing temperature of 95°C to complete the curing process and to provide a hard, strong plastic element.

The casting of the thermosetting plastic against a coated glass element is satisfactorily accomplished using the coated glass together with supplemental mould and gasket members to form a cavity into which the plastic in liquid form is poured or injected. One assembly suitable for this purpose is illustrated in Figure 1 of the accompanying drawings, which shows a thermosetting plastic-filled cavity defined by a mould a ring gasket and a curved sheet glass element having an interior thermoplastic coating. The curved sheet glass element is in turn supported by a second mould.

No specialized heating procedures are required for curing the thermosetting plastic while in contact with the coated glass. Thus, in a case where a diethylene glycol bis (allyl carbonate) resin is injected into the cavity, the filled mould assembly is placed in a curing oven and heated according to a time/temperature schedule conventional for the curing of such a resin.

One example of a suitable curing schedule, shown in Figure 2 of the accompanying drawings, comprises slow heating to a curing temperature of 95°C. over a time interval of 14 hours, after which the resin is essentially completely polymerized to a hard clear plastic element. The schedule shown is for a 4 mm thick "CR-39" plastic element combined with a polyvinyl butyral thermoplastic coating having a heat sealing temperature above the maximum plastic curing temperature of 95°C.

During the consolidation step which immediately follows the curing step, the cured plastic element, glass element and thermoplastic coating are consolidated by briefly heating them above the heat sealing temperature of the thermoplastic coating. This step is illustrated in Figure 2 of the accompanying drawings for the case of a polyvinyl butyral coating having a heat sealing temperature of about 120°C.

At temperatures below its heat sealing point, the polyvinyl butyral thermoplastic coating does not bond well to allyl diglycol carbonate plastic, so that stresses due to plastic shrinkage are largely

avoided. Such shrinkage may be substantial, as exemplified by the 14%, by volume curing shrinkage illustrated in Figure 3, of the accompanying drawings for a thermosetting allyl diglycol carbonate resin cured in accordance with the curing schedule of Figure 2.

At heat sealing temperatures, the soft polyvinyl butyral layer may flow to relieve any residual stress and permanently bond the asembly into an integral glass/plastic composite article. The only stress then present in the composite as it finally cooled to ambient temperature is that arising out of the differences in thermal expansion between the glass and plastic elements at temperatures below the softening temperature of the thermoplastic layer.

In certain preferred embodiments of the present invention, the adhesive is applied to the glass element in the form of a foil and a temporary release layer is applied to the foil on the surface opposite to the surface applied to the glass element and is removed prior to casting the thermosetting resin.

The following Examples illustrate the present invention.

EXAMPLE A

A glass element for a glass/plastic composite lens, consisting of a round, spherically-curved glass disc about 0.0254 cm (0.010") in thickness, having a diameter of 70 mm and a surface curvature of 6.25 dioptres, is thoroughly cleaned using acetone, deionized water and alcohol. A solution of polyvinyl butyral is prepared consisting of 10 parts plastic solids and 90 parts solvent, by weight. The solids component of the solution consists of 60% by weight, of "Butvar B-98" polyvinyl butyral powder, available from the Monsanto Company, and 40%, by weight, of "3GH" plasticizer, available from the Union Carbide Corporation. Ths solvent component of the solution consists of 22.5% diacetone alcohol, 22.5% *n*-butyl alcohol, 10% ethyl alcohol and 45% xylene, by volume.

The thus-prepared polyvinyl butyral solution is sprayed onto the concave surface of the curved glass lens element until a solid thermoplastic layer about 0.013 cm (0.005") thick is formed. The convex (uncoated surface) of the glass is then placed directly against a curved glass ceramic supporting mould, a thermoplastic rubber ring about 4 mm in thickness and having an inside diameter of about 60 mm is placed on the coated surface of the glass and the thus-provided open cavity is filled with prepolymerized "CR-39" thermosetting resin. The convex surface of a second curved glass ceramic mould is then placed over the resin and plastic gasket to form a closed cavity, substantially as shown in Figure 1 of the accompanying drawings.

This filled mould assembly is clamped, placed in a curing ov n and heated in accordance with the heating schedule shown in Figure 2 of the accompanying drawings, that heating schedule comprising controlled heating to 95°C over a 14 hour interval to cure the "CR-39" resin to a hard plastic, followed by heating to 120°C for 10 minutes to heat-seal the cured plastic to the polyvinyl butyral coating. Finally, the mould assembly is cooled at room temperature.

The mould assembly is opened and the consolidated composite lens removed and examined. The lens is of optical quality, free of glass and plastic defects and the curvature of the front (glass-clad) surface of the lens substantially conforms to the 6.15 dioptre curvature of the glass lens element used in fabrication.

EXAMPLE B

A glass lens element having a size and configuration essentially identical to the lens element described in Example A above is cleaned and positioned in a concave glass ceramic supporting mould as therein described. A clean sheet of thermoplastic polyvinyl butyral, consisting of a section of 0.0254 cm (10 mil) -thick "Saflex SR-10" polyvinyl butyral film, from the Monsanto Co., is placed over the glass element, covered with a thin sheet of polyethylene terephthalate acting as a release layer and finally covered with a 4.5 kg (10-lb.) weight having a curvature matching that of the supporting mould and glass lens element.

This assembly is placed in a vacum oven and heated at 120°C under a partial vacuum (71 cm (28")) of mercury) to remove trapped air from the assembly and to preliminary bond the polyvinyl butyral sheet to the glass lens element. It is then taken out of the vacuum oven and the weight and polyethylene terephthalate sheet are removed from the glass-thermoplastic sub-assembly.

This sub-assembly is then gasketed, filled with thermosetting "CR-39" resin, covered with a curved glass-ceramic mould, clamped, and thermally processed to achieve plastic curing and consolidation of the glass and plastic lens elements in accordance with the procedure described in Example A above. The composite lens produced by this process is again of optical quality, free of glass and plastic defects and having a front surface curvature corresponding to the initial curvature of the glass element used to form the front surface of the lens.

CLAIMS

1. A direct casting process for the production of a low-stress composite article comprising a glass element bonded to a high-shrinkage thermosetting plastic element which comprises:

– coating selected surface portions of the glass element with a thermoplastic adhesive having a heat sealing temperature above the minimum curing temperature of the thermosetting plastic;

– casting the thermosetting plastic in liquid form against the surface portions of the glass element which have been coated with the thermoplastic adhesive;

– curing the thermosetting plastic by heating the plastic, the glass element and the thermoplastic adhesive to a temperature below the heat sealing temperature of the thermoplastic adhesive, but above the minimum curing temperature of the thermosetting plastic;

and

– consolidating the cured thermosetting plastic, thermoplastic adhesive and glass element into a unitary glass/plastic composite by heating them to a temperature above the heat sealing temperature of the thermoplastic adhesive.

2. A process as claimed in claim 1 in which the glass element is up to 0.05 cm in thickness.

3. A process as claimed in claim 1 or claim 2 in which the thermoplastic adhesive is polyvinyl butyral.

4. A process as claimed in any of claims 1 to 3 in which the high-shrinkage thermosetting plastic is an allyl diglycol carbonate plastic.

5. A process as claimed in any of claims 1 to 4 in which the adhesive is applied to the glass element in the form of a foil.

6. A process as claimed in claim 5 in which a temporary release layer is applied to the foil on the surface opposite to the surface applied to the glass element and is removed prior to casting the thermosetting resin.

7. A process as claimed in claim 1 substantially as herein described.

8. A process as claimed in claim 1 substantially as herein described with reference to the Examples and/or accompanying drawings.

9. A composite article when produced by a process as claimed in any of claims 1 to 8.

10. An optical element or system which comprises a composite article as claimed in claim 9.

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